

Forum

Methane in Association With Seismic Activity

It has been hypothesized that upward movement of vast quantities of methane gas from the earth's mantle is a causative agent of earthquakes (Gold, 1979). Much of this hypothesis rests on accounts of flames and/or loud, booming noises ("bronzes") accompanying seismic events, possibly caused by the explosive release of this "primordial" methane to the atmosphere (Claffin-Chilton and MacDonald, 1978; Gold and Soter, 1979). This speculation has generated much controversy because it implies a nonbiological source of energy in the mantle (e.g., Nature, 1982; Eas, 1983). However, there is a paucity of experimental data to either support or contradict this hypothesis. Because of this continuing, unresolved controversy, I have decided to publish some observations made several years ago with respect to methane emanations during an earthquake that struck near Mammoth Lakes, Calif. (Oremland, 1979). It is of significance that this region lies in close proximity to Owens Valley where accounts exist of flames emanating from the ground during the 1872 earthquake (Claffin-Chilton and MacDonald, 1978; Gold, 1979).

One possible test of Gold's hypothesis would be the demonstration that dramatic releases of methane frequently accompany seismic activity. Although it does not necessarily follow that methane released during seismic events is of primordial origin (e.g., biogenic or thermogenic methane entrapped near the surface could be released by strong earth movements), the consistent presence or absence of unusual large plumes of methane in association with earthquakes would either lend support to or contradict the hypothesis, respectively. An earthquake of 5.7 magnitude (Richter) struck about 30 km south-east of Mammoth Lakes, California, at 9:45 A.M. on October 4, 1978 (for details see Savage and Clark, 1982). The depth of the epicenter was 13.6 km (R. Cokerhan, personal communication, 1983). The initial shock lasted several seconds, and a series of aftershocks of diminished intensity occurred for several hours thereafter. Eyewitnesses at Hot Creek, a geothermal stream having several fumaroles, reported the sudden release of large quantities of steam and gases at the time of the first shock. These emanations were of sufficient magnitude to panic the few bathers present, and park officials immediately closed the area. There were no observations of flames exiting the ground. Because I had established a record of the methane content of some of the Hot Creek gas seeps 57 days prior to the earthquake, and because the creek was studied previously with respect to its chemistry and gaseous emanations (Mariner and Wiley, 1974), it was possible to determine if any dramatic increase in the methane content of these geothermal gases occurred soon after the initial shock of this seismic event.

Table 1 lists the methane concentrations of two proximate gas seeps (A and B) and two large fumaroles (C and D). Seep A consisted of a slow trickle of bubbles (about 25 cc/min) emanating from warm sediments (50°C) located near the stream bank (water depth about 10 cm). Seep B was located about 1 m away in slightly deeper water (depth about 25 cm), had a faster gas flow rate (about 100 cc/min), and emanated from a more rocky bottom than seep A (sediment temperature = 50°C at seep B). Methane concentrations in the gases from both seeps were low and actually decreased somewhat with the arrival of the earthquake. These methane values are in agreement with the data of Mariner and Wiley (1974). Fumaroles C and D were located about 50 and 75 m, respectively, away from seep A and on the opposite stream bank. Prior to the quake,

they were senescent and demonstrated minimal gas ebullition (they were not sampled). However, after the first shock and for several subsequent days they violently

TABLE 1. Methane Concentration in Gases From Hot Creek Seeps (A and B) and Fumaroles (C and D)

Site	Percent Methane in Gas Phase		
	Sept. 17, 1978	Oct. 4, 1978	Oct. 9, 1978
A	0.16	0.12	0.12
B	0.07	0.06	ND
C	ND	0.01	0.01
D	ND	0.01	0.01

Gases were collected by displacement of water in a capped funnel. The collected gases (50 cc) were next drawn up into a syringe, and the contents were injected into sealed, vented serum vials (volume = 5 cc). Analyses were performed within 3 hours of sample collection. Collection of gases on Oct. 4, 1978, were made within 3 hours after the first shock. Samples were analyzed on a Varian series 1400 flame ionization gas chromatograph equipped with a Porapak Q column (305 x 0.64 cm; N₂ carrier flow = 30 cc/min). Limit of detection was about 0.0005%. ND = not determined.

extruded gas bubbles and silt. Fumarole C even spawned a 3 m high water geyser as a consequence of the earthquake. Therefore, new materials were being brought to the surface; however, the methane content of gases emanating from these hot fumaroles (water temperature = 82°C) was about an order of magnitude lower than that of the bubbles exiting the cooler seeps (Table 1). None of the gases collected was combustible.

The higher methane concentrations of the gases at seeps A and B were due to the presence of methanogenic bacteria in the warm and reducing sediments (they had an H₂S odor) surrounding the seeps. Thermophilic methanogenic activity is a common occurrence in hot springs (e.g., Ward, 1978), and anaerobic incubation of sediments taken near the seeps demonstrated abundant biological methane production at 62°C (Figure 1). Methanogenesis was blocked by addition of chloroform (Figure 1), an inhibitor of methanogenic

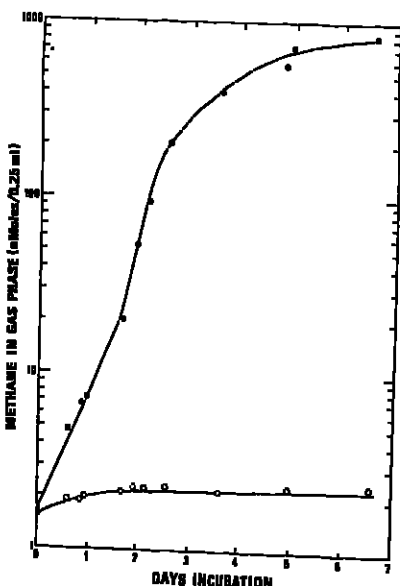


Fig. 1. Methanogenesis in Hot Creek sediments incubated statically in the dark at 62°C. Sediments were collected with a plastic core liner (upper 5 cm of sediment) from a warm (54°C) fumarole located near seeps A and B; 50 cc of sediment were placed into 250 cc Erlenmeyer flasks that contained 75 ml of fumarole water. Flasks were gassed with N₂ for 5 min and then sealed with black rubber stoppers. Open circles, flask containing 0.1 ml of chloroform; closed circles, uninhibited flask. Final methane levels achieved in the uninhibited flask (412 µmoles) corresponds to about 8% of the gas phase volume. Addition of 60 cc of H₂ to another uninhibited flask caused an immediate, seventeenfold stimulation of methane production rates (data not shown).

bacteria (Brauchop, 1967), and, in addition, methane production rates were stimulated seventeenfold by addition by hydrogen to the sediments (data not shown). The high temperatures at fumaroles C and D exceeded the physiological range of most thermophilic methanogens (Zeikus and Wolfe, 1972; Ward, 1978), and therefore the lower methane content of the fumarole gases was probably a consequence of these organisms being absent from those environments. Further evidence for the active presence of methanogenic bacteria near the seeps but not the fumaroles can be inferred from the presence of traces of hydrogen in the fumarole gases (0.03–0.07%) but not in the seep gases. Hydrogen is commonly associated with methanogenic gases (Lyon, 1974), and because it is a common substrate of methanogenic bacteria, it would be removed from gases that transit sediments harboring an active flora of these organisms.

It is therefore evident that increases in the methane content of geothermal gases did not accompany this earthquake and that methane remained a minor component of the gases. Furthermore, increases of methane were not observed during a 1974 eruption of the Kilauea volcano in Hawaii, and concentrations in collected gases remained below 1.4 ppm (R. Lamontagne, personal communication, 1983). It has been argued that one might not observe liberation of methane in volcanic regions if mineral-catalyzed oxidation of methane to carbon dioxide occurred (Gold, 1979). However, experimental evidence does not support this contention (Sackett and Chung, 1979). Furthermore, the oxidation reaction envisaged would have to operate at near 100% efficiency to account for the low methane values observed in Hot Creek and Kilauea, a feat that is difficult to achieve for a vast volume of methane quickly transiting a hot mineral region during an earthquake. Finally, as noted at the outset, Hot Creek lies in proximity to the region where accounts of flames escaping the earth were recorded during the Owens Valley earthquake of 1872 and were cited as supportive evidence for the methane "deep gas" hypothesis (Gold, 1979).

It should be noted, however, that methane can be an abundant component (i.e., >40%) of the gases of mud volcanoes (Reitsemann, 1979). In addition, significant levels of methane (about 2.5%) were observed in some of the gases collected during a 1977 Kilauea eruption (Graeber et al., 1979). In both cases, however, the investigators were able to attribute the source of the methane to pyrolysis of buried organic matter. I have observed a high methane content (about 11%) in gases exiting the mud-flow debris region on Mount St. Helens. However, the presence of both methane and propane in the gas as well as the fact that the site was located on top of 600 feet of hot, recently buried organic-rich debris lends further credence to a shallow pyrolytic origin (with perhaps a biogenic contribution as well) for the methane rather than a deep "primordial" one (R. S. Oremland, unpublished data, 1983).

The observations presented in this report contradict the methane "deep gas" hypothesis of Gold (1979). It must be stressed that any gases released during seismic events or along rift zones may become relatively enriched in methane because of contributions made by liberated pockets of ancient or recent methane entrapped within the crust. This gas may have been formed by biogenic (as in the case of Hot Creek) or thermogenic mechanisms occurring within the crust. Thus, observations of isotopically heavy methane (δ¹³C_{CH₄} = -20 to -15 per mil) in association with plumes of H₂ emanating from thermal regions (Welhan and Craig, 1979; Gutsalo, 1980; Lupton and Craig, 1981; Welhan et al., 1981) does not prove a mantle origin for the methane because the gas may have been "stripped" out of the crust with upward movement of H₂. Furthermore, identification of sources of methane that are based primarily on carbon isotopic composition of the gas can be clouded by the activities of methylotrophic bacteria which can enhance the ¹³C component of the methane (Silverman and Oyama, 1968; Barker and Fritz, 1981; Coleman et al., 1981]

and give it a thermogenic character. Such data, when used to identify sources of "primordial" methane, should be interpreted with caution.

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News

Volcanic Sulfur Dynamics

Gaseous sulfur in the aerosol clouds produced by the eruptions of Mount St. Helens and El Chichón is the current focus of research on the effects of matter injected into the atmosphere by volcanoes. Recent research shows that new particles of sulfuric acid are formed up to 3 months after an eruption and that these particles can continue to grow for more than half a year following an eruption. These sulfuric acid particles may alter the earth's climate by interfering with the transmission of radiation from the sun into the lower atmosphere and of infrared radiation from earth back out to space. Furthermore, evidence published last month claims that sulfur emissions during noneruptive phases may be the main source of volcanic sulfur in the atmosphere.

Although effects of sulfuric acid are minimal in the troposphere (which extends to approximately 16 km above the earth at the equator and to 9 km at the two poles), it causes measurable changes in the flow of radiation in the stratosphere (the next major

layer above the earth, ranging in thickness from 15 km at the equator to 50 km at the poles). Ongoing research aims to assess the complete impact of sulfur and its derivatives on the chemistry of the atmosphere. According to M. Patrick McCormick of the National Aeronautics and Space Administration (NASA), the May 1980 eruption of Mount St. Helens and the April 1982 eruption of El Chichón provided researchers with an experiment in nature at a time when there is sound technology with which to conduct investigations. The scale of this experiment is suggested by the volume of sulfur involved: The stratosphere was injected with approximately 7.5×10^7 kg of sulfur by the 1980 Mount St. Helens eruption (Eas, August 10, 1982, p. 601), and the 1982 El Chichón eruption infused an even greater amount, recent work shows.

Sulfuric acid (H₂SO₄) is the product that directly interferes with solar radiation. The amount of atmospheric H₂SO₄ formed from an injection of sulfur is a function of the sulfur's residence time in the atmosphere and the oxidation and hydration rates it undergoes there.

Although the exact conversion rate of sulfur to sulfuric acid is still under investigation, it is more rapid in the stratosphere than in the troposphere because of higher photochemical activity caused by stronger solar radiation at that level of the atmosphere. The oxidation process leading from sulfur to sulfur trioxide (S, SO, SO₂, SO₃) and the subsequent hydration to H₂SO₄ varies with the availability of water vapor, which fluctuates in different regions over the earth. (Most volcanic sulfur is injected into the atmosphere as sulfur dioxide.)

In 1981, A. S. Kabanov and S. S. Khmel'nikov, of the Experimental Meteorology Institute in the USSR, speculated on the mechanism of sulfate aerosol formation in the stratosphere. They proposed that droplets grow when sulfuric acid molecules adhere to existing water droplets, forming a stratospheric water vapor passes into the liquid phase.

By virtue of vertical mixing and water precipitation, the troposphere is cleansed of sulfur products much more quickly than the stratosphere. The residence time of sulfur products is measured in days to weeks in the troposphere, whereas it is 1–3 years in the stratosphere.

D. J. Hofmann and J. M. Rosen, reporting in *Geophysical Research Letters* in April 1983 on the amount and mass of sulfuric acid aerosol produced by El Chichón, concluded that new particles of sulfuric acid were formed for about 3 months after the eruption. When particle formation ceased, though, particle growth was evident 7 months after the eruption. Their observations, made with three balloon-borne optical particle counters, revealed two layers of aerosol particles in the stratosphere. The higher layer, located at 25 km, consisted of 80% sulfuric acid, while the lower layer, hovering around 18 km, consisted of 60–65% sulfuric acid, estimate the University of Wyoming scientists. Data also indicated possible partial depletion of water at 25 km because of the conversion of gaseous sulfur to sulfuric acid.

Foremost among the instruments used to measure aerosol dispersion is the light detection and ranging (LIDAR) remote sensing system. The device operates by shining light into space. Backscattering of the lightwaves by particles in the atmosphere produces an echo that is then compared with atmospheric heights, and a measure of the dispersion is then calculated. While unable to distinguish between specific compounds, LIDAR can determine the position and relative size of an aerosol cloud of volcanic origin.

Arlin Krueger, also of NASA, said that systems used to measure sulfur dioxide include the Total Ozone Mapping Spectrometer (TOMS) number 7 and the Solar Backscatter Ultra Violet (SBUV), both on the Nimbus-7 satellite. Although these instruments were designed to measure ozone, they can distinguish sulfur dioxide from ozone by the difference in the wavelengths of the radiative energy the compounds absorb. According to Krueger, the volume of sulfur dioxide measured by the systems employed by NASA is less than is implied by the size of the aerosol cloud; there may be a large, undetected volume of sulfur bound in another form, he said.

Following the 1980 eruption of Mount St. Helens, Alan R. Bandy of Drexel University and his colleagues embarked on project RAVE (Research on Atmospheric Volcanic Emissions), an effort by NASA and university scientists to investigate the detailed chemical nature of volcanic plumes. Research conducted by the team using the LIDAR system, among others, is expected to expand the basis for diagnosing the major processes in volcanism. In a 1982 paper, the team stressed that "better estimates of the magnitude and variability of volcanic emissions are required if the importance of this natural source of atmospheric constituents and the resulting effect on atmospheric chemistry and burdens of species are to be elucidated." An important result of a RAVE experiment (conducted by

repeatedly traversing the volcanic plume) reported in 1982 was the estimate of sulfur dioxide flux from Mount St. Helens as 9×10^4 kg/day on September 22, 1980.

The use of direct measurements of volcanically injected sulfur and a proposed classification of volcanic activity, including eruptive and noneruptive phases, are the main advantages of a new model that assesses atmospheric sulfur contributed by volcanoes, according to a paper in the April 20 *Journal of Geophysical Research*. H. Berresheim and W. Jaeschke of the Center for Environmental Protection at the J. W. Goethe-University, Frankfurt/Main, Federal Republic of Germany, argue in their paper that emissions of sulfur during noneruptive phases, previously neglected by researchers, are the main source of the volcanic sulfur in the atmosphere.

In the same issue, the University of Wyoming's Rosen and Hofmann report on the newly discovered quasiannual variation of concentrations of condensation nuclei. Condensation nuclei are liquid or solid atmospheric particles that initiate the condensation of vapors into aerosols. Although the team concludes that there is no single explanation for the variance of condensation nuclei concentration, it speculates that sulfuric acid resulting from recent eruptions may play a role. Rosen and Hofmann say that study of condensation nuclei, thought to be the link between precursor gases and aerosol formation, will aid in developing predictive models and understanding stratospheric aerosol chemistry.—MEG

Pioneer 10 Leaves Solar System

The National Aeronautics and Space Administration's (NASA) unmanned spacecraft, Pioneer 10, was expected to leave the outer reaches of our solar system on June 13, 1983. (The division between the solar system and outer space is defined as the edge of the sheath of influence of the solar wind; this sheath is called the heliosphere.) On its way to space beyond our solar system, Pioneer 10 will pass close enough to Neptune and Uranus to obtain data which may be useful in determining whether or not "Planet X" exists. Planet X is the hypothetical cause of Neptune's and Uranus' perturbed motion, so far unexplained by earth observation. In addition, as it leaves the heliosphere, scientists hope Pioneer 10 will map the apex of the solar wind teardrop.

Pioneer 10, launched on March 2, 1972, was intended to last for about 2 years. When Pioneer 10 leaves our solar system in June and heads into interstellar space, NASA will celebrate its success. Ceremonies will be held in the Capitol, the Ames Research Center where the Pioneer 10 project is being managed, and at TRW in southern California where the spacecraft was built.

Now the spacecraft is nearly 2.8 billion

miles from the sun. Tracking data are being obtained regularly and will continue to be received, even when it is twice as far from earth as it is now.—PMB

Combating Illiteracy

A science course for nonscientists at Columbia University's Columbia College that was created in 1981 as an experiment to combat "the national crisis of scientific illiteracy" has received major new foundation support and has achieved a prominent place in the college's curriculum.

The course, *The Theory and Practice of Science*, has received a \$240,000 grant from the Andrew W. Mellon Foundation, according to Robert E. Pollack, college dean, professor of biological sciences, and originator of the course. The grant will be used for the preparation and publication in 1983 of a textbook, titled *The Scientific Experience*, which will permit the course to be taught at other schools around the country.

The course is designed to expose students to the way in which scientists think and reach conclusions about the physical world, rather than to teach them the substance of only one discipline. The course "is unique," Pollack said. "It is not a history or philosophy of science, but a study of pure science, to show what scientists think is elegant about their subject." Pollack teaches the course with Herbert Goldstein, professor of applied physics and nuclear engineering, and Jonathan Gross, professor of mathematical statistics and computer science. Funds from the Mellon grant will enable the addition of four other faculty members and the addition of a second section of the course in the 1983–1984 academic year. More sections are planned for future years, Pollack noted. The four faculty joining the original core are Samuel Eilenberg, University Professor Emeritus; Darcy Kelley, associate professor of biology; David Helfand, associate professor of physics; and Robert Crease, philosophy instructor.

The course, which began with 15 students and funding from the Exxon Education Foundation and an anonymous donor, doubled in size in the 1982–1983 academic year with a grant from the Atlantic Richfield Foundation.

NEXRAD Negotiations

Two firms have been selected for negotiation for preproduction models of NEXRAD, the next generation weather radar system, that aims to improve severe weather forecasting. The 40-month, cost-plus-fixed-fee con-

News (cont. on p. 412)

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Article (cont. from p. 409)

Also recognizing that improved satellite techniques can resolve many small-scale oceanographic problems, we recommend the development of space instrumentation with at least an order of magnitude improvement in accuracy and the incorporation in the space systems of ancillary instruments to measure such phenomena as sea state, sea surface temperature, ice, salinity, and color, and further recommend that these space programs be undertaken on regional and global scales on a continuous basis.

Finally, recognizing the need for additional surface and subsurface measurements in solving oceanographic and geologic problems, we recommend that an ocean monitoring system and data han-

dling facility be developed and implemented concurrently with the satellite system.

Tsunamis

To improve the reliability of tsunami prediction, we recommend development of a deep-water system to measure tsunami wave height in real time. This system would provide a supplemental parameter to the tsunami warning system and would be of immense use if a failure of the tide gauge systems occurs, as it did in the December 1979 tsunami.

Conclusion

After the technical recommendations, the panel urged that a study be made to investigate the economic benefit-to-cost ratio for

each specific recommendation, and concluded with the following proposal:

Since marine geodetic programs are distributed within several federal agencies, which due to duplication of programs waste user's time to locate a right agency for obtaining information, we strongly recommend that a dynamic group be formed to conduct marine geodetic program direction; this group should be within one federal agency and responsive to all ocean applications programs. This group should be advised by all segments of the involved scientific and user community in the tradition of the Office of Naval Research and the National Aeronautics and Space Administration.

